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Effect of Low Impurities of Oxygen in Inert Gas and its Pressure on the Surface Tension of Liquid Indium

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Abstract—The effect of oxygen impurities in argon and helium and their pressure in the range of 10^{-4} Pa to 15 MPa on the surface tension of liquid indium is studied using the method of maximum pressure in a gas bubble. It was shown that the presence of oxygen in an inert gas results in an increase in the surface tension of indium with increasing pressure.

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INTRODUCTION

Investigating the interaction of gases with the metal surfaces is of fundamental importance in solving a wide range of basic and applied problems. Among the numerous works concerned with the experimental study of surface tension (ST, σ) of metals at different interfacial boundaries, there are rare works in which the experimental data on a metal's ST are given in dependence on the pressure of the gas phase over their surface [1, 2]. Of the more recent publications, we can mention [3], where it was found that the grain boundary energy of tricrystalline aluminum of 99.999% purity varies from 0.53 to 0.62 J/m^2 in the pressure range of 0 to 14 kbar.

It was shown that under conditions of multiphase equilibrium, the contact angle of organic liquids on an aluminum substrate increases in proportion to the pressure of the vapor phase [4]. Study of the effect of partial pressure of oxygen on the surface tension of liquid Sn–Ag alloy at 1253 K showed that coefficient $(d\sigma/dp)_T$ has a minimum value at an Ag molar fraction of 0.9 and an oxygen partial pressure of 10^{-13} atm [5].

However, there are theoretical studies in which not only the dependence of the ST of metals on the gas pressure over their surface was proposed, but also the corresponding calculations based on the thermodynamic analysis using the method of a layer of finite thickness were given [6, 7]. It was shown that the interfacial energy at the metal–low soluble gas boundary increases with increasing pressure. This regularity was confirmed experimentally for nonmetallic liquids [8]. On the other hand, another regularity has been observed in a number of studies [9–13]. In particular, the surface energy was estimated within the context of the statistical electron theory [9–11], and by using the electron-density functional method [12] as well as other techniques [13–15]. In these works, the data from calculations are given, according to which the ST of metals should decrease with increasing pressure of the gas phase at their surface.

It was therefore of interest to study the processes at a liquid metal–gas interface. This work deals with the experimental investigation of the influence of low impurities of oxygen in inert gas and its pressure on the ST of liquid indium.

EXPERIMENTAL

The ST of liquid indium was measured on a multipurpose experimental installation made of Kh18N10T stainless steel and designed for studying the interfacial interactions at a liquid–gas medium boundary. It allowed us to perform measurements in the pressure range of 10^{-4} Pa to 15 MPa at temperatures from room temperature to 600 K (Fig. 1). Chamber *1* of the experimental installation is a hollow, thick-walled cylinder with two sides and top and bottom flanges. Observation windows *3* made of optical glass 30 mm thick with PTFE seals are set in side flanges *2*, which seal the chamber over the pressure range.

Bottom flange *4* has fittings for thermocouple input *5*, current input *6* for an electromagnetic pin, and connection *7* to a vacuum pipe. On top flange *8* there are fittings *9* for supplying gas into the chamber and into instrument *10*, the removal of gas *11* from the chamber, fixing the instrument *12*, and an emergency pressure relief valve.

The top and bottom flanges along with all fittings have trench-wedge seals through an aluminum gasket. Inside the chamber is device *13* for measuring σ, tube *14* with the investigated metal, and a system of capillaries, through which the molten metal passes for removal of oxides before being loaded into the measuring device. The chamber is placed in an air thermostat with a fan/stirrer operating at temperatures ranging from room temperature to 600 K.

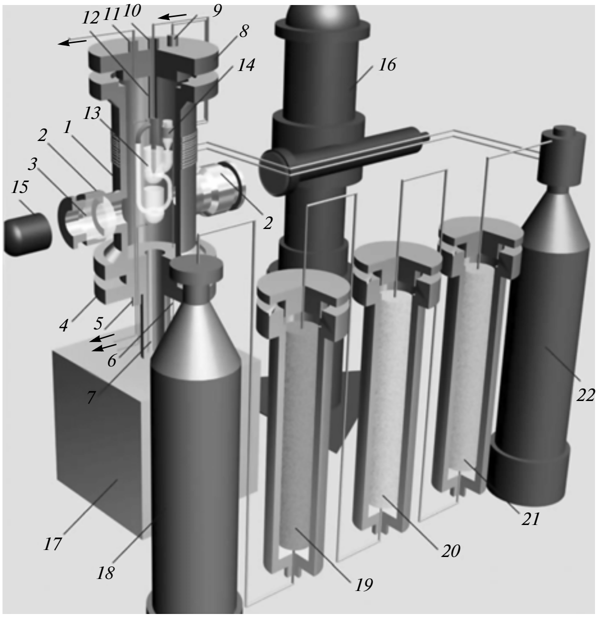

Fig. 1. Scheme of the installation for studying interfacial interactions at a liquid metal–gas medium boundary.

The temperature in the chamber it is adjusted and kept at a given level automatically using two thermocouples located at different height levels, with an absolute error of less than 0.1 K. For lighting the chamber, we used illuminator *15*; the value of the maximum pressure in a bubble was determined by cathetometer *16*. Vacuum part *17* of the installation consists of zeolite and magneto-discharge pumps, and enables us obtain a nonlubricant vacuum of 10^{-4} Pa in the chamber. A pressure of inert gas sufficient for the experiments was created using gas cylinder *18*. The gas line includes a system for fine purification of inert gases with high-pressure columns *19*, *20*, and *21*; balloon *22* to collect the purified gas; standard manometers of high pressure; and valves for fine adjustment of the pressure in the system.

To create an inert atmosphere in the chamber, we used argon and helium of high purity (TU 2114-002-05758954) [16]. The argon and helium were purified in various ways. The first purification stage was the same for argon and helium: the gas was passed under pressure through degassed zeolite NaX. The second stage for helium was activated carbon at the temperature of liquid nitrogen; for argon, a titanium tube or magnesium turnings at T = 900 K. The best results were obtained with argon bubbling through molten magnesium. The analysis of gas for the oxygen content was performed using Mugdan's method with a detection limit of approximately 0.0002 vol % of O_2.

The ST of indium was measured using the method of maximum pressure in a gas bubble on P.P. Pugachevich's modified gas instrument [17]. Inside the measuring instrument (made of molybdenum glass instead of a conventional glass capillary), we used a capillary made of stainless steel with finely honed edges (the thickness of the edge was about 1% of the smaller diameter of the capillary). The maximum pressure in a bubble expressed by the height of the investigated liquid column was determined using a V-630 cathetometer with an absolute error of less than 10 microns. ST was calculated using the Cantor formula with two members:

$$\sigma = \frac{1}{2} grH(1 - \frac{2}{3}\frac{r}{H})(\rho^{(\alpha)} - \rho^{(\beta)}), \quad (1)$$

where g is gravitational acceleration, r is capillary radius, H is the maximum pressure in a bubble expressed by the height of the investigated liquid column, and $\rho^{(\alpha)}$ and $\rho^{(\beta)}$ are the densities of the liquid and gas phases, respectively (at a given pressure).

When measuring the ST by the method of maximum pressure in a gas bubble, the mechanical vibrations of the entire installation, the thermal uniformity of the gas supplied to the instrument, and the temperature fluctuations in the chamber have a great affect on the measuring accuracy. The whole installation was mounted on a massive steel plate laid on a concrete foundation over a sand pad; for thermostatting the gas coming into the instrument, the chamber was wound with 3 m of gas pipeline. The ST was measured with no vertical temperature gradients in the chamber.

Our study of indium–argon and indium–helium systems was conducted at a constant temperature of T = 448 K. The purity of indium used in the experiments was 99.999 wt %; helium of grade B contained 99.99 vol % of the main substance without additional purification, and argon of grade A, 99.990 vol %. Indium ST was determined with a relative error not exceeding 0.2%. The values of maximum pressure in a gas bubble used for calculations of the surface tension of indium were determined by statistical processing of the data from five measurements at constant T and p using Student's t-test at a confidence level of 95%. The pressure of inert gas was first determined using a vacuum gauge (at pressures of 5×10^{-4} to 10 Pa), and then using a standard manometer with the relative error of ~1%.

RESULTS AND DISCUSSION

The results are presented graphically in Fig. 2. After processing the experimental data by the method of least squares, the following equations connecting the surface tension σ of indium with the gas pressure p at various oxygen concentrations were obtained:

1. In–Ar system (0.001 vol % O_2), σ = 562.7 + 2.0126p. The surface tension was measured in mJ/m^2 and the pressure in MPa;

2. In–Ar system (0.0005 vol % O_2), σ = 570.7 + 0.6936p;

3. In–He system (0.0004 vol % O_2), σ = 572.6 + 0/689p;

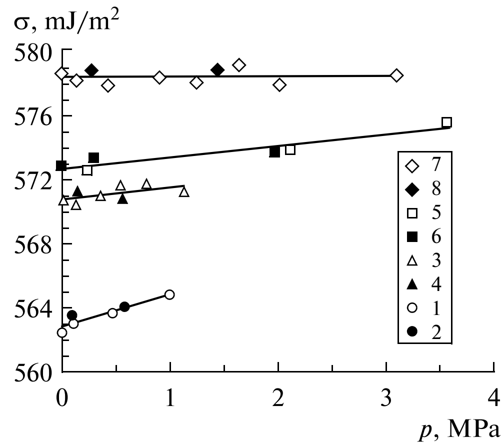

Fig. 2. Effect of pressure (in the process of raising and lowering) on the surface tension of liquid indium: (*1*) Ar + 0.001 vol % O_2 (raising), (*2*) 1 Ar + 0.001 vol % O_2 (lowering), $\sigma = 562.7 + 2.0126p$; (*3*) Ar + 0.0005 vol % O_2 (raising), (*4*) Ar + 0.0005 vol % O_2 (lowering), $\sigma = 570.7 + 0.6936p$; (*5*) He + 0.0004 vol % O_2 (raising), (*6*) He + 0.0004 vol % O_2 (decreasing), $\sigma = 572.6 + 0.689p$; (*7*) Ar + 0.0002 vol % O_2 (raising), (*8*) Ar + 0.0002 vol % O_2 (lowering), $\sigma = 578.3 + 0.0306p$.

4. In–Ar system (0.0002 vol % O_2), $\sigma = 578.3 + 0.0306p$.

The relative error of the determination of coefficient $(d\sigma/dp)_T$ for all systems was in the range of 30–40%.

The above equations allow us to follow the effect of oxygen concentration on the initial value of indium σ (at $p = 5 \times 10^{-4}$ Pa) as along with coefficient $(d\sigma/dp)_T$. The change in the oxygen content in inert gas from 0.001 to 0.0002% raised the ST by 15 mJ/m^2 and a lowered the slope of the σ(*p*) dependence by almost two orders of magnitude. The results can be explained by the occurrence of a heterogeneous reaction on the surface of the molten metal. Earlier, Auger spectroscopy showed that in the very deep vacuum on the surface of liquid metals there is an adsorption layer of carbon that is almost impossible to eliminate by thermovacuum treatment [16]. In our experiments, when the liquid metal was in contact with inert gas, there was additional adsorption of active impurities, as was indicated by a drop in σ with increasing concentrations of active ingredients in the inert gas. Later, the reaction of formation of carbon-containing molecules followed by desorption occurred, leading to an rise in σ with increasing *p*.

CONCLUSIONS

(1) It was shown that the dependence of the surface tension of indium on the pressure of inert gas (Ar and He) is linear.

(2) The oxygen content in gas affects the slope of the σ(*p*) dependence. The slope decreases with decreasing oxygen content in the inert gas.

(3) The above regularity was explained by the heterogeneous reaction of carbon-containing molecules, followed by desorption on the surface of liquid indium; this led to an rise in σ with increasing pressure.

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